

Management of Time-Sensitive Chemicals Part III: Stabilization and Treatment

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Introduction

In two previous articles we discussed how there are many misconceptions concerning time-sensitive chemicals (1, 2) and how time-sensitive chemicals should be managed. What remains to be discussed is “How does one treat and stabilize time-sensitive chemicals that have been stored for prolonged periods and have developed additional hazards?” That is the subject of this manuscript. (Note: For the purpose of this manuscript, the term “expired chemical” will refer to any time-sensitive chemical that has been stored for prolonged periods and has developed additional hazards that must be mitigated.)

Whenever an expired chemical is found, it must be treated in order to be rendered safe for disposal, further use, etc. Several steps are involved in this process. First, one needs to identify potential hazards. Second, determine how they can be mitigated. Third, necessary equipment and reagents for the process need to be identified and procured. This means the work needs to be clearly understood and carefully planned. The fourth step is the identification of the personnel who will perform the task and the last step is the actual treatment of the product that would include readying it for final dispositioning.

Hazard Identification - If it has happened, then it must be possible

Assumptions used in the process to determine hazards may appear to be contrary to those typically used when performing chemical research. One assumption used in performing chemical research is that the information is not valid or publishable unless it can be repeated. The assumption that must be made in the area of treating time-sensitive chemicals to render them safe is similar to “If it has happened, then it must be possible”. If a reaction is reported to have occurred, then it must be assumed to be able to occur again. There are several reasons for this assumption. One reason is that the source term is undefined. Once a container is sealed, one does not know anything about the conditions inside the container prior to the next opening. One does not know if the product inside is dry, if the vapor concentration is too rich or lean to burn, if oxygen is present, if the “goo” present in the ground glass joint is grease or hazardous product, etc. A second reason is that one never really knows if hazard mitigation efforts (e.g. wetting dried picric acid in the threads of the cap) have been successful until after the container has been opened. A third reason is that many “events” have been reported involving time-sensitive chemicals. These “events” may be explosions involving peroxides, toxic products that have accumulated over time which have led to exposures, container over pressurizations that led to container failure, etc. Many times, exact conditions and chemistry of what occurred are unknown. If conditions inside the container that need to be stabilized and rendered

safe are unknown as were those conditions inside a similar container that was reported to be involved in an event, then the behavior of the container during stabilization cannot be predicted. For this reason, all potential hazards must be treated as being present, unless, it can be proven, without a doubt, they are not present. If it happened once, then it must be assumed to be able to happen again. Because of this assumption, one must always be conservative when treating time-sensitive chemicals to render them safe.

Work Planning

Once potential hazards have been identified, the work needs to be planned so that it can safely be performed. The work plan will define equipment and reagents needed. For example, a glovebox needs to be present if the work needs to be performed in an anaerobic environment. If an exothermic reaction is possible, then ice or some other cooling materials should be present. If fire is a possibility, then provisions need to be made to control any potential fire. If an energetic reaction is possible, then provisions such as working in a fume hood, behind a blast shield, working remotely, etc., should be evaluated. Provisions should always be made to ensure workers have the proper personal protective equipment (PPE). Proper PPE could include ballistic fragmentation suits, self contained breathing apparatuses (SCBAs) (with extra breathing air cylinders), face shields, gloves, eye protection, flash suits, etc.



Figure 1. Sample PPE: flash suit, face shield, SCBA.

One concept that should be followed is to ensure more than enough necessary equipment and reagents are obtained to perform the task given any foreseeable situation. For critical items such as cooling ice, fire

extinguishers, etc., there should be a substantial excess present. It should be noted that previous reports have shown how measured peroxide concentrations can be in error and indicate substantially lower levels than actually present (2). In these situations, neutralization will involve more peroxides than that measured. This will result in much more heat than initially anticipated being released, which will require much more cooling (e.g., excess ice) to keep the reaction under control.

Another issue that should be addressed in the work planning stage is where the work will be performed and how the time-sensitive chemicals will be transported to that location. Areas where the work can be performed need to be identified and several considerations are involved in the decision of where this should be. One consideration is if the work could be performed at the work location without endangering other activities or workers. Another consideration would address potential hazards associated with transporting the time-sensitive chemicals to the work area. If the product is dangerous to move, then the possibility of treating it where it is currently located should be evaluated. If a potentially dangerous product must be moved, then it should follow a path that would provide a minimum of risk to others. Movement and treatment of potentially dangerous products could also be performed after hours or on a weekend to minimize the hazard to other workers. Another consideration involving the identification of a suitable work area involves the size and accessibility. Work areas should not be cramped because a small work area will tend to make any fires, explosions, toxic releases, etc., worse for those present. Also, cramped work areas make it more difficult to stage necessary equipment and supplies. If a temperature excursion is observed and ice is not immediately and easily available due to the cramped conditions, then there is a greater chance of losing control of the reaction. Cramped work areas are much more difficult for responders should an upset condition occur. Emergency responders wearing SCBAs and other protective gear have a very difficult time moving about in cramped areas. These difficulties will slow their response and exacerbate consequences. Lastly, the potential work location should be evaluated to determine its proximity to safety showers and eyewash stations, support equipment, other hazardous work, etc. Surrounding structures need to be assessed to determine the size of exclusion zone needed. For example, cement walls and cement block structures require a minimal exclusion zones, while wood or glass structures may require a more expansive ones. Exclusion zones typically used are a “Hot Zone” where work is being performed; a “Warm Zone” for logistic support; and a “Cold Zone” for safety support and access control.

Training, experience and other qualifications of individuals involved in the treatment and stabilization of time-sensitive chemicals is another element of work planning. All work needs to be closely supervised by a person who has an in depth understanding of the chemistry of the product being treated. This person needs to be present at all times so that they are available should something unexpected occur. Additionally, workers should have extensive experience in working with chemicals and equipment while dressed out in associated PPE. The process of treating and stabilizing time-sensitive chemicals should be considered and treated as being an elevated risk operation and not a place for novices or for those who are learning the equipment. In the event of an upset, it is imperative that the employees be well versed on how the

equipment and PPE function so that they know how to properly react. Training that helps provide a foundation for the necessary experience could include OSHA 40 hour HAZWOPER training, HazMat 40 hour technician training, care and use of remote handling equipment, chemistry and chemical techniques, SCBA certification training, etc. Additionally, workers and supervision should be well versed on the chemistry of those products that they are going to treat and stabilize. Lastly, the amount of training (including apprenticeship) and experience necessary should be proportional to the degree of hazard associated with the treatment and stabilization work. Relatively simple work like that described later in this article can be performed by readers with a fair amount of training and skill while other processes such as neutralizing ethers containing peroxides should be left up to professionals. If there is any question about the skill and training level necessary to perform this work, then always choose the most conservative. This decision would also include when one would decide to hire a contractor to perform the work.

Treatment/Stabilization Processes

The following are a few examples and not to be taken as procedures for stabilization and treatment processes. These examples have been picked to demonstrate how the process should work and to provide an idea as to the amount of precautions that are necessary to perform the work safely. It should be noted that there are many kinds of time-sensitive chemicals and that treatment and stabilization processes for each is different. The examples provided are for relatively simple tasks that could be performed by experienced laboratory workers under the supervision of a chemist.

Cellulose Nitrate

Cellulose nitrate is cellulose that has been nitrated and the degree of hazard is related to the degree of nitration - the greater the degree of nitration, the greater the hazard. Legacy nitrocellulose may be found as old motion picture film stock. Nitrocellulose is typically sold in several different forms. It can be sold as a thick strip called “bark”, which is treated as a flammable solid. It can also be sold as a wetted fibrous product that increases the flammability hazard should the wetting agent evaporate. Lastly, it can be sold as a solution. Numerous solvent mixtures such as those containing diethyl ether, tetrahydrofuran, amyl acetate, etc., can be used and, when sold as a solution, may go by other names such as “collodian” or “parlodian”. Nitrocellulose can become a time-sensitive chemical when it is either purchased as a solution or is dissolved into solution at the place of work. Nitrocellulose solutions can be stored in bottles that have either a screw top cap or a ground glass top. If the nitrocellulose is used and a portion comes in contact with either the bottle threads or the ground glass joint, then the solvent can evaporate over time and form a thin film. This thin film can become friction sensitive such that opening the container will cause the thin film to ignite. While this reaction would not normally be sufficient to cause the container to explode, it would be sufficient to ignite the flammable solvents present in the container. (The assumption made in this

example is that the nitrocellulose is not dissolved in a solvent such as diethyl ether or tetrahydrofuran. These solvents can form peroxides over time which would be an additional hazard requiring a different stabilization/treatment process.)

In order to safely open containers of nitrocellulose dissolved in a solvent, one must ensure that any nitrocellulose present on the threads of the bottle or in the ground glass joint is wetted with solvent. Solvent that is present to wet the nitrocellulose will act as a lubricant and will render the nitrocellulose thin film less sensitive to friction. Wetting the threads or the joint of the bottle will reduce or eliminate the potential for a dangerous reaction to occur. The preferred method for wetting the threads or the ground glass joint would be to invert the container in a reservoir using sufficient solvent to ensure that the threads or glass joints are completely covered. The reservoir should be covered to prevent evaporation of the solvent. A desiccator jar with its lid can work well for this procedure. Most solvents used have a low viscosity, therefore, little time is required to wet the threads or glass joint. Usually one hour will be sufficient, however, one may choose to allow an overnight soaking to ensure complete wetting when the threads cannot be easily seen.

Once the threads or glass joints are wetted, the lids may be removed. Precautions should still be taken to ensure that a container does not ignite upon opening. Several methods are available to perform this task. One method would be to attach clamps to both the bottle and the lid and then bury the bottle in vermiculite or some other nonflammable packing material. Once buried, the clamps can be used to remove the lid. If there is an initiating spark, then the packing material will prevent a fire by preventing air from coming into contact with the container. A disadvantage to this process is that absorbent material can become contaminated with the organic solvent and nitrocellulose resulting in more material that would need to be discarded. A similar method would be to open the containers under water. The disadvantage to this method is the potential contamination of the water with the organic solvent and nitrocellulose. A third, and likely the best, method would be transferring the container to an inert atmosphere glove box and opening the container inside the glove box using the clamps. The glovebox would provide physical protection from a minor explosion and the inert atmosphere would ensure that a fire involving air trapped inside the container is not sustainable. An advantage to this method is that there would be no possibility of contaminating other products such as packing materials or water, which would complicate clean up and disposal.

Since the most hazardous portion of the work has been completed at the point the container is opened, the work would be transferred to a fume hood where manipulations can more easily be carried out. Container contents can then be poured into a large, plastic, wide-mouth bottle. Sometimes the solution will be too viscous to pour. When this occurs, more solvent can be added to reduce the viscosity. Extra solvent should be used to rinse out bottles that contained the nitrocellulose solutions and the rinsate added to the plastic

bottle. Eventually, by adding more solvent, the concentration of the nitrocellulose in the solvent should be reduced to less than 1% before sealing and sending off as waste for disposal.

There are a few qualifiers for this process. First, this method is not intended for use on nitrocellulose containers that are larger than 100 ml. Second, this method should NOT be used when diethyl ether, tetrahydrofuran, or any other peroxidizable solvent is involved. Experts should be brought in to perform the work under either of these circumstances. Third, the resulting solution should not be stored for a considerable time before dispositioning it as waste. This method should be coordinated with a waste dispositioning company so that the treated nitrocellulose can be removed shortly after it has been processed.

Sodium Metal

Sodium metal can react with oxygen over time to form sodium superoxide (Figure 2). The superoxide of sodium appears as a black coating on the surface of the metal and is a very strong oxidizing agent that can react violently with organic materials. Due to its reactivity, waste disposal is not an option until the hazard has been mitigated.



Figure 2. Note the dark patches of sodium superoxide (3).

Of the many methods available for neutralizing sodium superoxide, converting it to sodium alkoxide is one of the easiest and safest. This method involves reacting the superoxide/sodium metal with an alcohol to form sodium alkoxide and hydrogen gas. Despite being a “safe” method for treating superoxide-contaminated sodium, it still requires extreme caution.

This procedure is performed in a 5 or 10 liter flask or container with an orifice large enough to introduce the metallic sodium/sodium superoxide. Borosilicate glass is the material of choice for the container since

it is resistant to corrosive materials such as sodium ethoxide, impervious to solvents such as ethanol, and can tolerate elevated temperatures. The ideal reaction vessel would be a two neck, 5 or 10 liter, round bottom flask with 24/40 ground glass joints modified to have a large opening capable of introducing the sodium (see Figure 1). Provisions also must be made to allow for a thermometer, condenser, and a means for introducing an inert gas flow. If a round bottom flask described above is to be used, then a three neck Claisen adapter would work well. (Note: One of the arms of the Claisen adapter would have a two neck Claisen adapter present to provide a means for adding additional ethanol should the need arise.)



Figure 3. Setup for converting sodium superoxide to sodium alkoxide

Equipment should be set up in a fume hood and firmly clamped together as shown in Figure 3. The bottom of the flask should rest upon a magnetic stirrer such that a Teflon® coated stir bar can turn freely inside the flask. One arm of the Claisen adapter should have a condenser attached. Ice water should be pumped from a 5-gallon pail into the condenser and extra ice should always be available. The condenser must be kept as cold as possible. An inert gas such as argon or nitrogen is required to sweep away any hydrogen that is formed and to keep the atmosphere in the reaction vessel inerted. Care must be taken to ensure that the flow of gas does not become excessive (> 2 SCF/hour) during the reaction. A 200°C thermometer should

be inserted into another arm of the Claisen adapter while dropping funnel is placed upon the last arm of the Claisen adapter. This dropping funnel will contain the ethanol that will be used in the reaction.

Personnel who will be performing the neutralization activities (especially cutting of the sodium) need to wear appropriate PPE. The PPE would include at a minimum SCBA, body armor, full-body Kevlar® coveralls, Nomex® hood, full flash cover, Kevlar® and nitrile gloves and heavy flash gloves. Additionally, a class ABC fire extinguisher should be available. When sodium metal cutting is being performed, then a class D fire extinguisher or bucket of sand should be available and the buddy system should be used.

Once the apparatus is set up, the process can begin. The first step is to place the sodium into the flask. Sometimes the sodium will be present in pieces that are too large to be used. These large pieces need to be cut into smaller pieces. To do this, the sodium should be removed from the mineral oil using laboratory tongs and placed in a Pyrex® baking dish that has sufficient mineral oil present to cover the sodium metal. The sodium can then be cut into smaller pieces using a knife. (Some chemical references will report that this cutting method could result in explosions, but this claim applies only to potassium metal.) Remove a piece of sodium (Approximately 50-75 grams each) from the mineral oil by gently grasping it with laboratory tongs and quickly placing it (without dropping it) in the reaction flask. (Care should be taken not to grasp part of the sodium that has a heavy coating of superoxide present.) Replace the lid covering the orifice used to place the sodium into the reaction flask, allow the atmosphere to become inerted and lower the fume hood sash to the point where maximum air velocity is attained. Ethanol in the dropping funnel should then be freely added until the sodium is covered. The reaction should begin as soon as the ethanol touches the metal. As the reaction proceeds, the sodium will float to the top of the solution and, at this point, the stirrer should be started. As the reaction proceeds, an off white film will form on the surface of the solution and the temperature may increase noticeably. More ethanol should be added to cool the reaction and to ensure the sodium and the superoxides have been completely consumed. The reaction is complete when there are no pieces of sodium floating in the solution and the temperature has cooled below 90°C (approximately 1 hour). At this point the mixture can be removed from the flask using due caution since the sodium ethoxide will be extremely corrosive. It can quickly cause severe skin burns or attack active metals such as the aluminum on an aluminized flash suit cover. Subsequent batches can be run using the same flask until all sodium metal has been treated.

Conclusions

As can be seen by the above two examples, the treatment and stabilization of time-sensitive chemicals requires safety measures that are far above that normally required for typical laboratory work. There is good reason for these conservative measures.

To begin with, these are not routine tasks for most laboratory technicians or chemists. The required training and PPE are generally not available. Also, the participants are typically not skilled in the subtleties of the treatment processes. For these reasons one should not attempt to treat time-sensitive chemicals unless the treatment is elementary or unless one is very experienced in the treatment process. If one is not experienced in these treatment processes then one should contract with a professional service.

As can be seen by this and the two proceeding manuscripts in this series (1, 2) on time-sensitive chemicals, it is very important to properly manage time-sensitive chemicals. In the first manuscript (1) we showed how dangerous time-sensitive can become and in this manuscript we have shown how dangerous it can be to render them safe by treatment. These two issues amplify the importance of time-sensitive chemical management as was described in the second manuscript (2).

Managing these types of chemicals should not be a process of ignoring them until you have to address them. A program needs to be in place whereby the minimum required is purchased, storage and handling are well defined, training is adequate, a disposal path is in place before the chemical is purchased and allowed to develop additional hazards, and has full and unwavering management support.

References:

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